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**WO 03/006563 A1**

(54) Title: **A COMPRESSED FLUID FORMULATION**

(57) Abstract: An imaging composition comprising a mixture of a fluid and a functional material; wherein the fluid is compressed and the functional material is dispersed and/or solubilized in the compressed fluid; and wherein the mixture is thermodynamically stable or thermodynamically metastable or both.

## **A COMPRESSED FLUID FORMULATION**

### **FIELD OF THE INVENTION**

This invention relates generally to imaging compositions that  
5 contain functional materials that are dispersed and/or solubilized in a fluid that is  
in a compressed state. The compositions are used to create a high-resolution  
pattern or image onto a substrate.

### **BACKGROUND OF THE INVENTION**

In a typical ink jet recording or printing system, ink droplets are  
10 ejected from a nozzle towards a recording element or medium to produce an image  
on the medium. The ink droplets, or recording liquid, generally comprise a  
functional material or functional material, such as a dye or pigment or polymer,  
and a large amount of solvent. In conventional inkjet printing systems, the liquid  
ink droplets are ejected from the nozzle using pressure pulses generated by an  
15 oscillating piezoelectric crystal or by heating the nozzle to generate an ink droplet  
resulting from bubble formation or from ink phase change. The solvent, or carrier  
liquid, typically is made up of water, an organic material such as a monohydric  
alcohol, a polyhydric alcohol or mixtures thereof. There can be many additives in  
the system aimed at preserving the pixel integrity upon deposition to the receiver.  
20 Such materials may be surfactants, humectants, biocides, rheology modifiers,  
sequestrants, pH adjusters, and penetrants among others. Such materials are  
necessary due to the high water loads in conventional ink formulations

Technologies that deposit a functional material such as a toner  
particle onto a receiver using gaseous propellants are known in the prior art. For  
25 example, Peeters et al., in U.S. Pat. No. 6,116,718, disclose a print head for use in  
a marking apparatus in which a propellant gas is passed through a channel, the  
functional material is introduced controllably into the propellant stream to form a  
ballistic aerosol for propelling non-colloidal, solid or semi-solid particulate or a  
liquid, toward a receiver with sufficient kinetic energy to fuse the marking  
30 material to the receiver. There is a problem with this technology in that the  
functional material and propellant stream are two different entities and the

propellant is used to impart kinetic energy to the functional material. This can cause functional material agglomeration leading to nozzle obstruction and poor control over functional material deposition. Another problem with this technology is that when the functional material is added into the propellant stream in the channel it forms a non-colloidal ballistic aerosol prior to exiting the print head. This non-colloidal ballistic aerosol, which is a combination of the functional material and the propellant, is not thermodynamically stable. As such, the functional material is prone to settling in the propellant stream, which in turn, can cause functional material agglomeration leading to nozzle obstruction and poor control over functional material deposition.

Thermal dye transfer printers use a transfer ribbon made of a plastic film. Page-sized panels on the ribbon consist of cyan, magenta and yellow dye in a solid form. A thermal print head, consisting of thousands of heating elements, capable of precise temperature variations, moves across the transfer ribbon. Heat from the heating elements cause the color on the ribbon to vaporize and diffuse onto the surface of the specially coated paper. Precise temperature variations are responsible for the varying densities of color. The hotter the heating element, the more dye is vaporized and diffused onto the paper's surface. Problems with this technology include the functional material, which is solid and is converted into gas, then deposited on the surface of the receiver. Also, thermally unstable materials cannot be used in the donor sheet. The receiver must be specially designed for the dye sublimation printing and include materials, which may require an overcoat for protection. This process requires a separate step in that the formulation needs to be coated separately via a curtain-coating process on to a transfer ribbon or substrate, which is then used in printing.

Technologies that use supercritical fluid solvents to create thin films are also known. For example, R.D. Smith in U.S. Patent 4,734,227, issued March 29, 1988, discloses a method of depositing solid films or creating fine powders through the dissolution of a solid material into a supercritical fluid solution and then rapidly expanding the solution to create particles of the functional material in the form of fine powders or long thin fibers which may be

used to make films. There is a problem with this method in that the free-jet expansion of the supercritical fluid solution results in a non-collimated/defocused spray that cannot be used to create high-resolution patterns on a receiver. Further, defocusing leads to losses of the functional material. There is yet another problem with the Smith method in that very few materials can be completely dissolved in supercritical fluid solutions, and this restricts the use of many common materials used in various applications, which are not soluble in supercritical fluids.

A different approach for marking is needed—one that would eliminate the need for the "water management" additives. There is also a need for a technology that permits high speed, accurate, and precise deposition of a functional material on a receiver. There is also a need for a technology that permits functional material deposition of ultra-small (nano-scale) particles. There is also a need for a technology that permits high speed, accurate, and precise patterning of a receiver that can be used to create high-resolution patterns on a receiver. There is also a need for a technology that permits high speed, accurate, and precise patterning of a receiver having reduced material agglomeration characteristics.

### SUMMARY OF THE INVENTION

The present invention overcomes the problems discussed above by providing an imaging composition comprising a mixture of a fluid and a functional material. The fluid is compressed and the functional material is dispersed and/or solubilized in the compressed fluid. The mixture is thermodynamically stable or thermodynamically metastable or both.

The present invention also provides an imaging composition comprising a mixture of a carbon dioxide and a colorant. The carbon dioxide is compressed and the colorant is dispersed and/or solubilized in the compressed carbon dioxide. The mixture is thermodynamically stable or thermodynamically metastable or both. The invention is useful for inkjet, organic light emitting diode display, color filter arrays, coating applications, polymer filler, and thin film formation applications.

The present invention discloses:

An imaging composition comprising a mixture of a fluid and a functional material;

wherein the fluid is compressed and the functional material is dispersed and/or solubilized in the compressed fluid; and

5 wherein the mixture is thermodynamically stable or thermodynamically metastable or both.

### BRIEF DESCRIPTION OF THE DRAWINGS

In the detailed description of the preferred embodiments of the invention presented below, reference is made to the accompanying drawings.

Figure 1 is a photomicrograph of lines drawn using compressed fluid formulation containing Duasyn Acid blue AE-02 ® dye used in the present invention. The dashed lines are produced with widths of approximately 100-200 microns.

15 Figure 2 is a photomicrograph of lines drawn using compressed fluid formulation containing Duasyn Acid blue AE-02 ® dye used in the present invention. The dashed lines are produced with lengths of approximately 1.2-5 millimeters.

Figure 3 is a photomicrograph of dots drawn using compressed fluid formulation containing Duasyn Acid blue AE-02 ® dye used in the present invention. The dots are produced with widths of approximately 2 millimeters.

### DETAILED DESCRIPTION OF THE INVENTION

The formulations useful in the present invention contain a functional material, which is dispersed and / or solubilized, in a compressed fluid. The compressed fluid is any material with a density greater than 0.1 grams/cc. The compressed fluid may include a compressed liquid and /or a supercritical fluid. Materials that are at sufficiently high temperatures and pressures below their critical point are known as compressed liquids. Materials in their supercritical fluid and/or compressed liquid state that exist as gases at ambient conditions find application here because of their unique ability to solubilize and/or

disperse functional materials of interest in the compressed liquid or supercritical state. In this context, the chosen materials taken to a compressed liquid and/or supercritical fluid state are gases at ambient pressure and temperature. Ambient conditions are preferably defined as temperature in the range from -100 to +100 °C, and pressure in the range from  $1 \times 10^{-8}$  - 100 atm for this application. More commonly, the ambient conditions are temperature in the range of 0 to 100°C and pressure in the range from  $1 \times 10^{-5}$  to 100 atm. for this application. One skilled in the art should know how to select and maintain the appropriate ambient conditions such that the selected compressed fluid is gas at the ambient conditions.

10                   The compressed fluids include, but are not limited to, carbon dioxide, nitrous oxide, ammonia, xenon, ethane, ethylene, propane, propylene, butane, isobutane, chlorotrifluoromethane, monofluoromethane, sulphur hexafluoride and mixtures thereof. Due its characteristics, e.g. low cost, wide availability, etc., carbon dioxide is generally preferred in many applications.

15                   Functional materials can be any material that needs to be delivered to a receiver, for example imaging dyes, ceramic nanoparticles etc., to create a pattern on the receiver by deposition, etching, coating, other processes involving the placement of a functional material on a receiver, etc.

20                   The functional materials may be selected from species that are ionic and/or molecular of the types such as organic, inorganic, metallo-organic, polymeric, oligomeric, metallic, alloy, ceramic, a synthetic and/or natural polymer, and a composite material of these previously mentioned. The functional material can be a solid or a liquid. Additionally, the functional material can be an organic molecule, a polymer molecule, a metallo-organic molecule, an inorganic molecule, 25 an organic nanoparticle, a polymer nanoparticle, a metallo-organic nanoparticle, an inorganic nanoparticle, an organic microparticles, a polymer micro-particle, a metallo-organic microparticle, an inorganic microparticle, and/or composites of these materials, etc. After suitable mixing with the compressed fluid the functional material is uniformly distributed within a thermodynamically 30 stable/metastable mixture, that can be a dispersion, with the compressed fluid.

Additionally, the functional materials can be functionalized to dissolve, disperse and/or solubilize the functional material in the compressed fluid. The functionalization may be performed by attaching fluorocarbons, siloxane, hydrocarbon functional groups to the electroluminescent material.

5                    Additionally, the ratio of surfactant to functional material in the formulation is from 0.1:1 to 500:1. More preferably, the ratio of surfactant to functional material is from 1:1 to 100:1. In yet another preferred embodiment of the invention, the ratio of co-solvent to functional material in the formulation is from 0.01:1 to 100:1. In still another embodiment of the invention, the ratio of  
10   compressed fluid to functional material in the formulation is from  $1:1 \times 10^5$  to 1:20.

                    Additionally, the formulation may contain a dispersant and or a surfactant to solubilize and/or disperse the functional material. The dispersant and/or surfactant can be selected from any group that will have appropriate  
15   solubility in the compressed liquid and/or supercritical fluid medium as well as have interactions with the functional material so that the functional material can be solubilized. Such materials include, but are not limited to, fluorinated polymers such as perfluoropolyether, siloxane compounds, etc. The surfactants preferred in the invention include Fluorolink 7004® (Ausimont Montedison Group) and  
20   Fomblin MF-300 ® (Ausimont Montedison Group).

                    The compressed fluid forms a continuous phase and the functional material dispersed and/or solubilized in the compressed fluid forms a single phase. The formulation is maintained at a temperature and a pressure suitable for the functional material and the compressed fluid used in a particular application.  
25   More commonly, the formulation conditions are temperature in the range of 0 to 100°C and pressure in the range from  $1 \times 10^{-2}$  to 400 atm. for this application.

                    The method of preparing the formulation will now be discussed. The apparatus used for making the formulation has been disclosed in the pending U.S. application Serial No. 09/794,671, which is incorporated here in its entirety.  
30   Briefly, the functional material is controllably introduced into the formulation reservoir. The compressed fluid is also controllably introduced into the

formulation reservoir. The contents of the formulation reservoir are suitably mixed using mixing device to ensure intimate contact between the functional material and compressed fluid. As the mixing process proceeds, functional material is solubilized or dispersed within the compressed fluid. The process of dissolution/dispersion, including the amount of functional material and the rate at which the mixing proceeds, depends upon the functional material itself, the particle size and particle size distribution of the functional material (if the functional material is a solid), the compressed fluid used, the temperature, and the pressure within the formulation reservoir. When the mixing process is complete, the mixture or formulation of functional material and compressed fluid is thermodynamically stable/metastable in that the functional material is dissolved or dispersed within the compressed fluid in such a fashion as to be indefinitely contained in the same state as long as the temperature and pressure within the formulation chamber are maintained constant. This state is distinguished from other physical mixtures in that there is no settling, precipitation, and/or agglomeration of functional material particles within the formulation chamber unless the thermodynamic conditions of temperature and pressure within the reservoir are changed. As such, the functional material and compressed fluid mixtures or formulations of the present invention are said to be thermodynamically stable/metastable.

The method for delivering the formulation to a suitable receiver will now be discussed. The apparatus used for delivering the formulation to a suitable receiver has been disclosed in the pending U.S. application Serial No. 09/794,671, which is incorporated here in its entirety. Briefly, the functional material is precipitated from the compressed fluid by manipulating and or changing the temperature and/or pressure conditions. The precipitated functional material is directed towards the receiver as a suitable shaped stream. The compressed fluid containing the functional material will be expanded through a suitable orifice into an ambient atmosphere where the compressed fluid will become a gas. The functional material will begin to precipitate non-reactively into particles and/or agglomerates of particles with the dispersant and/or surfactant



coating the surfaces of these particles and/or agglomerates thereby limiting the growth of particles. The precipitated and/or aggregated functional material, free of compressed fluid, is deposited on a receiver in a precise and accurate fashion to form a desired image. Hence the receiver is instantaneously dry upon delivery of the functional material on the receiver.

The receiver can be any solid including an organic, an inorganic, a metallo-organic, a metallic, an alloy, a ceramic, a synthetic and/or natural polymeric, a gel, a glass, and a composite material. The receiver can be porous or non-porous.

The size of the precipitated nanomaterials can be controlled by the ratio of functional material to dispersant and/or surfactant. The size of the precipitated nanomaterials can be controlled by the depressurization step through suitable orifice design and optimization with temperature of solution, pressure of solution, flow rate of solution, and concentrations of the functional materials and dispersant and/or surfactants. The size of the precipitated nanomaterials can be controlled by the appropriate selection of dispersant and/or surfactant material such as the type of functional groups on the molecule as well as the solubility in the particular compressed liquid and/or supercritical fluid. Typical particle size of the functional material deposited on the receiver is in the range of 1 nanometer to 1000 nanometers. More preferably, the particle size of the functional material is in the range of 1 nanometer to 100 nanometers.

The precipitated nanomaterial can also be collected by any number of methods. For example, the precipitated nanomaterials may be injected into/onto a suitable substrate sheet for immobilization or the nanomaterials may be collected in a suitable liquid. Due to the surfactant coating of the nanomaterials during the depressurization process, the nanomaterials will be stable and not undergo significant agglomeration. Thereby, discrete nanoparticles can be obtained depending on the processing conditions.

It is to be understood that elements not specifically shown or described may take various forms well known to those skilled in the art. Additionally, materials identified as suitable for various facets of the invention, for

example, functional materials. These are to be treated as exemplary, and are not intended to limit the scope of the invention in any manner.

### EXAMPLES

#### **Example 1 Preparation of a formulation containing Duasyn Acid Blue AE-02**

5    ® dye

0.01 g of Duasyn Acid Blue AE-02 ® (Clariant Corp.) and 0.649 g of Fomblin MF-300 ® (Ausimont Montedison Group) (Formula II) and 6.82 g of CO<sub>2</sub> (Matheson Group) were placed in a high-pressure cell at 23 °C and the pressure was adjusted to 204 atm (3000 psig). Visual examination of the view cell  
10    suggested that the formulation in the system was a homogeneous, single phase. This was further confirmed when the cloud point of the system was determined to be at 86 atm.(1258 psig).

#### **Example 2: Preparation of another formulation containing Duasyn Acid Blue AE-02 ® dye with a different surfactant**

15    0.01 g of Duasyn Acid Blue AE-02 ® (Formula III) and 0.649 g of Fluorolink 7004 ® (Formula I) (Ausimont Montedison Group) and 6.82 g of CO<sub>2</sub> (Matheson Group) were placed in a high pressure cell at 40 °C and the pressure was adjusted to 150 atm. Visual examination of the view cell suggested that the formulation in the system was a homogeneous, single phase.

#### **20    Example 3: Preparation of another formulation containing Copper Pthalocyanine, an Inkjet Functional Material**

0.0126 g of Copper Pthalocyanine (Formula IV), 0.4763 g of Fluorolink ® 7004, and 7.06 g of CO<sub>2</sub> were placed in a high pressure cell at 25.3°C and at 150 atm and mixed. After an appropriate time, the system was visibly homogeneous. The  
25    formulation was expanded to ambient condition through a needle valve for 5 seconds.

#### **Example 4: Writing a line using the formulation prepared in Example 2 (with lower frequency actuation)**

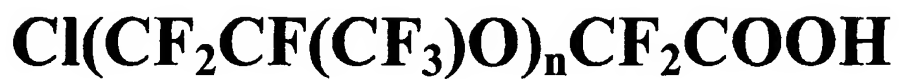
The formulation from Example 2 was kept at 150 atm and 40 °C in the  
30    formulation reservoir. This formulation is expanded through a nozzle, with a 300 micron throat. The nozzle was actuated at 30 Hz. The distance between the exit

of the nozzle and the substrate is set at a gap of 500 micron. A substrate translation speed of 2 inches/ second was used. Figure 1 shows the resulting dashed lines produced with widths of approximately 100-200 microns. Figure 2 shows the resulting dashed lines produced with lengths of approximately 1.5-2 millimeters.

**Example 5: Imaging dots using the formulation prepared in Example 2 (with higher frequency actuation)**

The formulation from Example 2 was kept at 150 atm and 40 °C in the formulation reservoir. This formulation is expanded through a nozzle, with a 300 micron throat. The nozzle was actuated at 150 Hz. The distance between the exit of the nozzle and the substrate is set at a gap of 500 micron. A substrate translation speed of 2 inches/ second was used. Figure 3 shows the resulting dots produced with widths of approximately 2 millimeters.

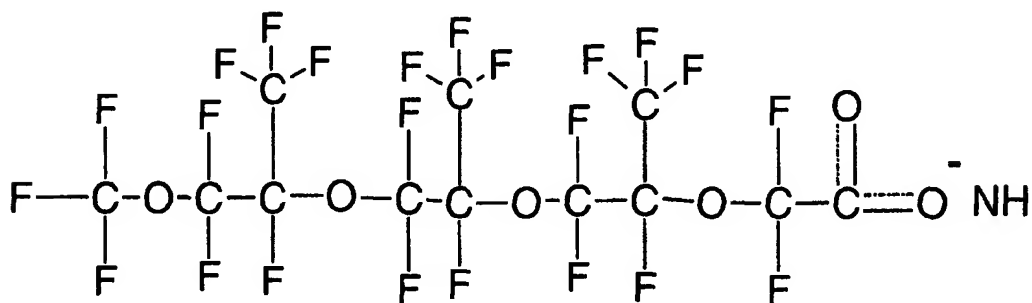
**Formula I:** Chemical structure of surfactant Fluorolink 7004 ® used in the present invention



5

10

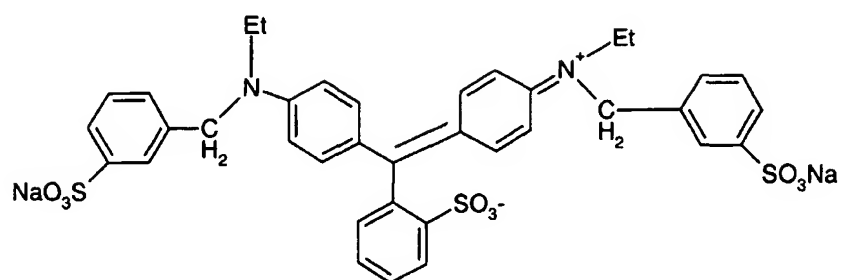
**Formula II:** Chemical structure of surfactant Fomblin MF-300 ® used in the present invention



15

**Formula III:** Chemical structure of Duasyn Acid blue AE-02 ® dye used in the present invention

5

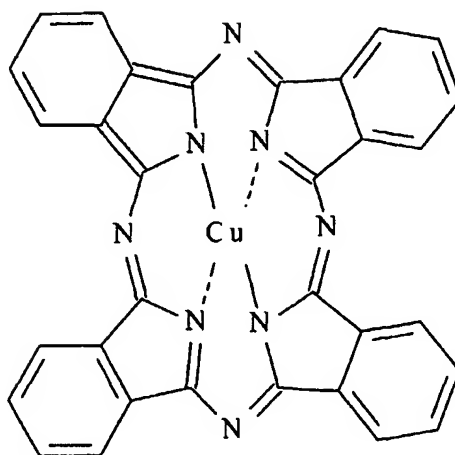


**Duasyn Acid Blue AE-02  
(Acid Blue 9)  
MW ~ 793 g/mol**

10

15

**Formula IV:** Chemical structure of copper pthalocyanine used in the present  
5 invention



**WHAT IS CLAIMED IS:**

1. An imaging composition comprising a mixture of a fluid and a functional material;

wherein the fluid is compressed and the functional material is dispersed and/or solubilized in the compressed fluid; and

wherein the mixture is thermodynamically stable or thermodynamically metastable or both.

2. The imaging composition according to Claim 1, wherein the fluid is a mixture of compressed liquid and supercritical fluid.

3. The imaging composition according to Claim 1, wherein the fluid is selected from the group consisting of carbon dioxide, nitrous oxide, ammonia, xenon, ethane, ethylene, propane, propylene, butane, isobutane, chlorotrifluoromethane, monofluoromethane, and sulphur hexafluoride.

4. The imaging composition according to Claim 1, wherein the functional material is selected from the group consisting of an organic molecule, a polymer molecule, a metallo-organic molecule, an inorganic molecule, an organic nanoparticle, a polymer nanoparticle, a metallo-organic nanoparticle, an inorganic nanoparticle, an organic microparticles, a polymer micro-particle, a metallo-organic microparticle, an inorganic microparticle, and a composite material.

5. The imaging composition according to Claim 1, wherein the functional material is imaging dyes, imaging pigments, ceramic nanoparticles, magnetic nanoparticles or semiconductor nanoparticles.

6. The imaging composition according to Claim 1, wherein the functional material is particulate.

7. The imaging composition according to Claim 1, wherein the mean particle size of the functional material is between 1 nanometer and 1000 nanometers.

8. The imaging composition of Claim 1, wherein the ratio of compressed fluid to functional material is from  $1:1 \times 10^5$  to 1:20.

9. An imaging composition comprising a mixture of a carbon dioxide and a colorant;

wherein the carbon dioxide is compressed and the colorant is dispersed and/or solubilized in the compressed carbon dioxide; and

wherein the mixture is thermodynamically stable or thermodynamically metastable or both.

10. An imaging composition comprising a mixture of a fluid and a functional material;

wherein the fluid is compressed and the functional material is an electroluminescent material which is dissolved, dispersed and/or solubilized in the compressed fluid; and

wherein the mixture is thermodynamically stable or thermodynamically metastable or both.



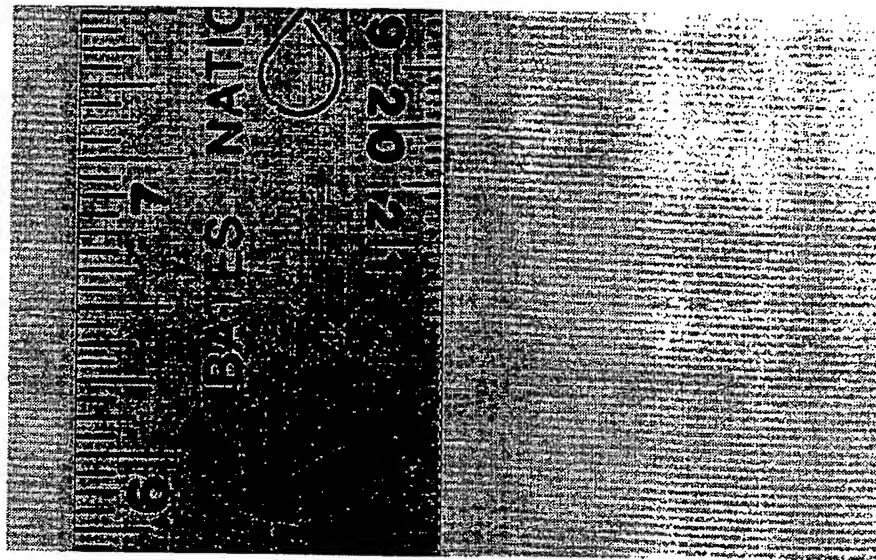


Fig. 1

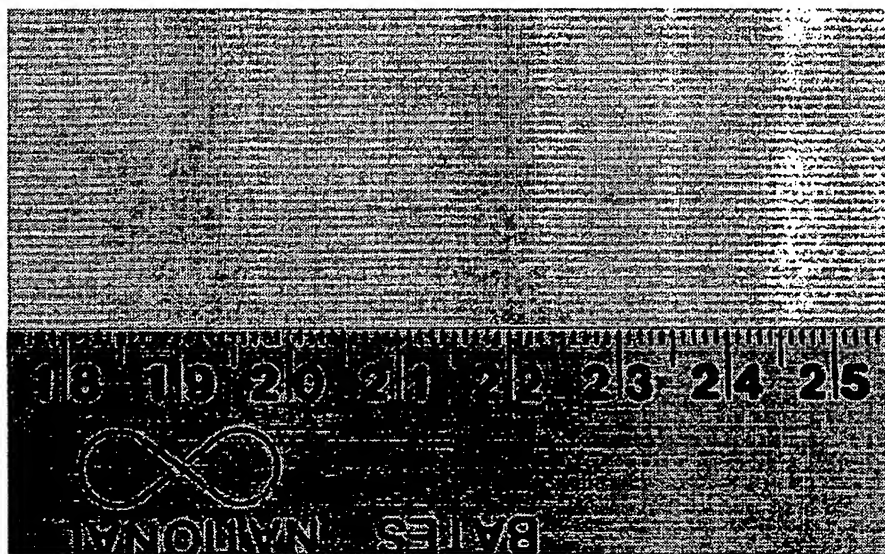


Fig. 2

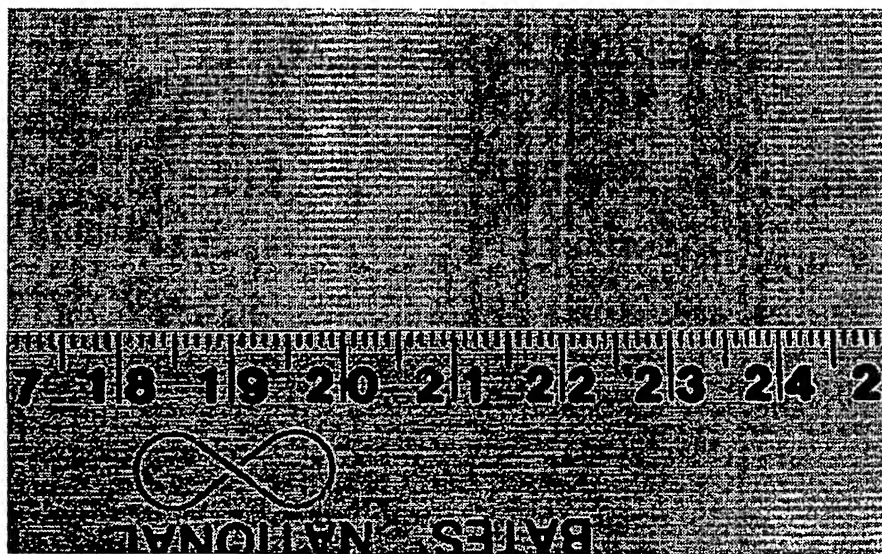


Fig. 3

## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 02/21789

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09D11/02 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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